DIRECT SELF-ASSEMBLY OF CHOLESTERIC LIQUID CRYSTAL POLYESTERS ON SILICON SURFACES BY SOLVENT CASTING TECHNIQUES

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OVERVIEW

Optoelectronic Cholesteric Liquid-Crystal-Polymers (ChLCP), synthesized in our lab [1], Fig. 1., when dispersed in solution, self-organize on metal surfaces, such as: Si(111); Pt/TiO2 / SiO2 /Si(001), Ag, Au, either colloidal spheres or thin layers [2].

Their HELICAL MACROMOLECULES, Figure 2, uncoil and get adsorbed on the metal via π-interaction, with the aromatic rings extended parallel to the interface and the aliphatic chains directed towards the bulk solution, according to the scheme depicted in Figure 3.

Figure 2. PTOBDME helical molecular model

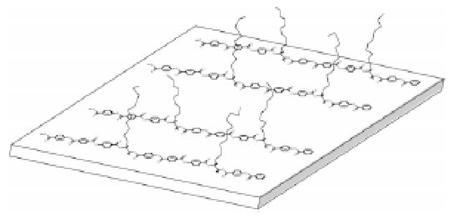


Figure 3. Adsorption of extended PTOBDME on Ag thin layer

Issues

Under spin coating controlled conditions growth, PTOBEE and PTOBDME have been obtained in multilayer ordered structures on Si and Pt substrates.

AFM images, Fig.9, Fig.10 and Fig.11 show polymer aggregates ~200 nm size in diameter, homogeneously dispersed on the Pt metal surface, and 200-400 nm on the Si (111) substrate.

We are interested in studying the growth morphology (shape, height and size) of these aggregates, as well as their optical, electrical and tribological properties.

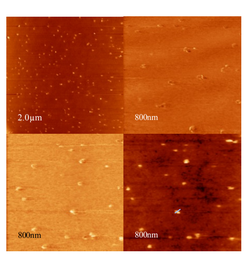


Figure 9. PTDOBDME on Pt / TiO2 / SiO2 /Si(001)

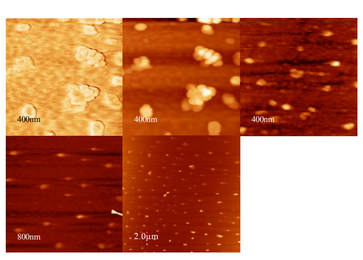


Figure 10. PTDOBDME on Si(111).

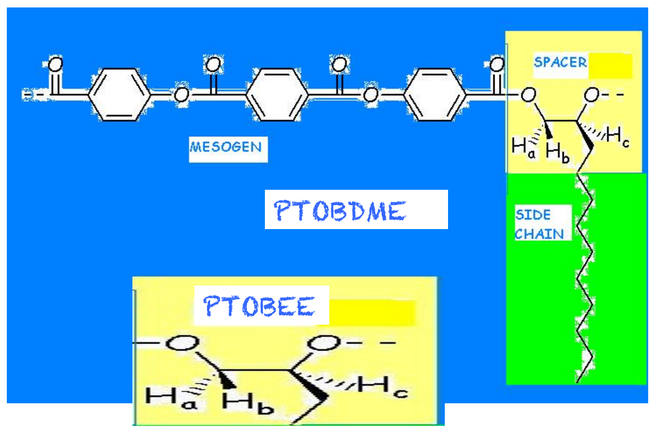


Figure 1. Schematic formula of **C**holesteric **L**iquid **C**rystal polymers PTOBDME and PTOBEE with the same mesogen and spacer, but different side chain.

These synthetic CHOLESTERIC LIQUID-CRYSTAL POLYMERS, exhibit OPTICAL ROTATORY DISPERSION (ORD), COMPLEX CIRCULAR DICHROISM (CD) patterns, TRANSMITANCE and REFLECTANCE.

EXPERIMENTAL OPTICAL PROPERTIES

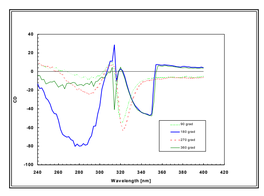


Figure 4. CD of PTOBEE thin solid film, rotated each 90°.

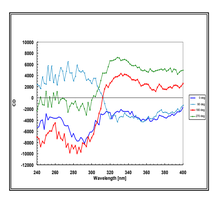
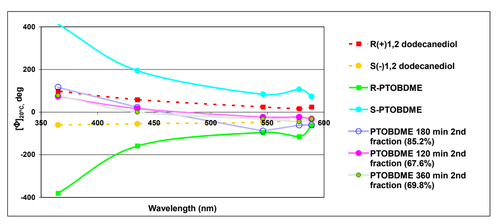
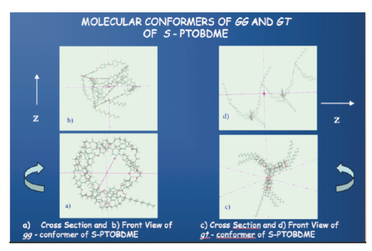


Figure 5. CD of PTOBDME



(a)



(b)

Figure 6. (a) Molar Optical Rotation [Φ] of Chiral ChLC Polymers: R-PTOBDME, S-PTOBDME, synthesized from R(+)1,2 dodecanediol, S(-)1,2 dodecanediol;
and
several fractions of PTOBDME, synthesized from racemic D,L-1,2 dodecanediol, under different kinetics, with distinct principal helical conformational models *gg* or *gt* obtained by NMR **(b)**, according to [8]

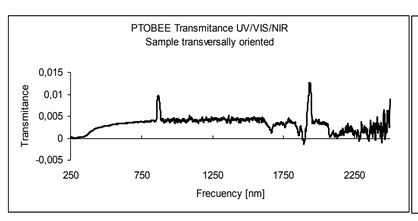


Figure 7. Transmitance of ChLCP PTOBEE

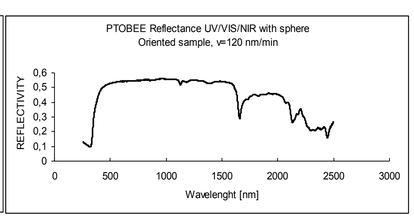
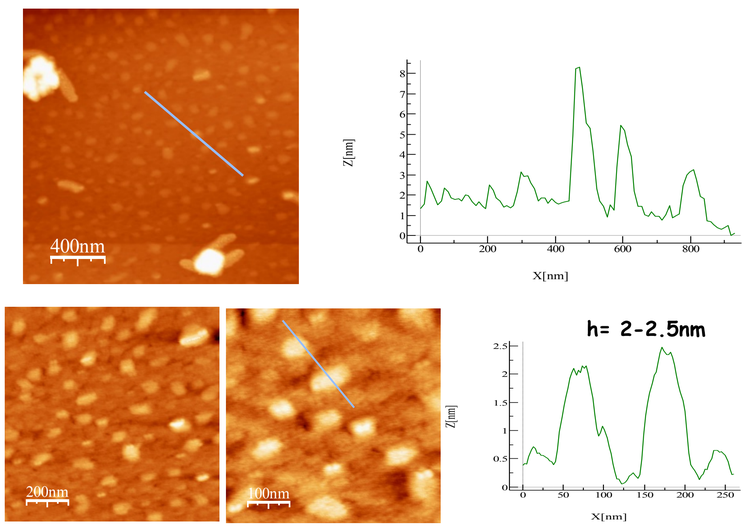
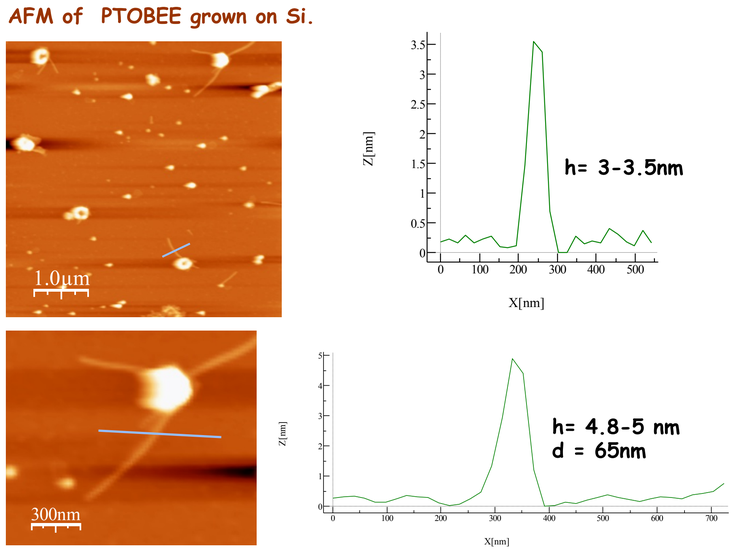


Figure 8. Reflectance of ChLCP PTOBEE

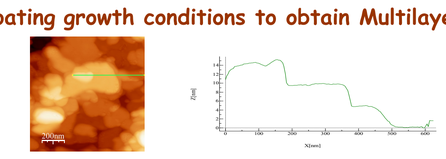
Figure 11. AFM CHARACTERIZATION of PTOBDME grown on Si



AFM of PTOBEE grown on Si.

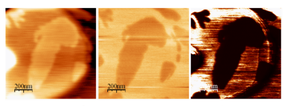


- Optimization of dip coating growth conditions to obtain Multilayered Structure of ChLC Polymer



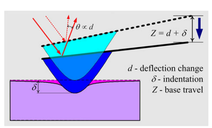
-Nanotribologic characterization: adhesion, friction and wear in controlled humidity environments

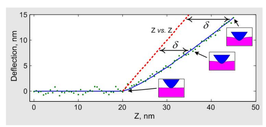
-Conductivity measurements

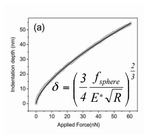


Topography Friction Current

-Elasticity (Young's modulus) and conductivity measurements, according to [3], [4].







CONCLUSIONS

Spin coating of the ChLC polymers dispersed in alkyl-alcohol media leads to the formation of round or ring-shaped aggregates on the semiconductor surface. By using a dip coating technique, both polymers assemble into layered deposits via multilayer growth of two-dimensional islands, evidencing the existence of step edge barriers to downward mass transport. In addition, we have found a variation of the step height with each layer deposited, consistent with a progressive decrease of the molecules tilt relative to the surface normal. The ChLC-polymer/semiconductor surface interaction mechanism has been further investigated by means of molecular mechanical (MM) models, matching simultaneous small and wide angle X-ray scattering (SAXS/WAXS) experiments performed with synchrotron radiation monochromatic beam (1.5 Å) and NMR spectra. Both simulations and experiments support an atomic self-organization of the cholesteric liquid-crystals on the Si surface due to an amphiphilic non-covalent interaction, consistent with the specific morphological features observed by AFM.

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